Rapid detection and characterization of surface CO_2 leakage through the real-time measurement of $\delta^{13}C$ signatures in CO_2 flux from the ground

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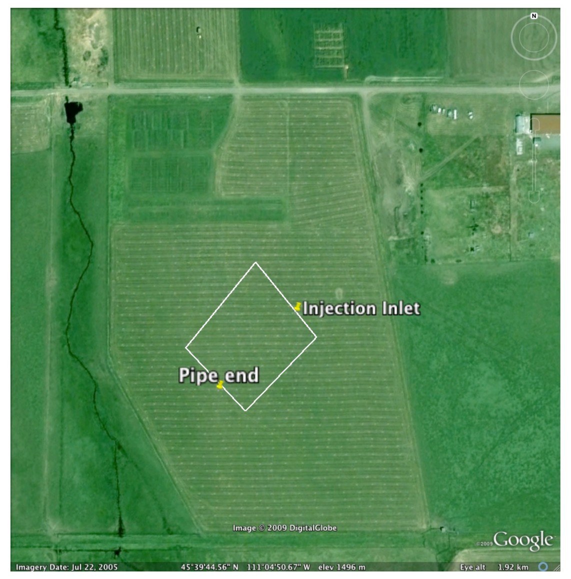
Introduction

A portable stable carbon isotope ratio analyzer for carbon dioxide, based on wavelength scanned cavity ringdown spectroscopy, has been used to detect and characterize an intentional leakage of CO2 from an underground pipeline at the ZERT experimental facility in Bozeman, Montana. Rapid (1 hour) walking surveys of the 100m X 100m site were collected using this instrument. The resulting CO2 concentration and 13-C isotopic abundance maps were processed using keeling plots permitting the identification of specific leakage locations and the ability to distinguish petrogenic sources of CO2 from biogenic sources.

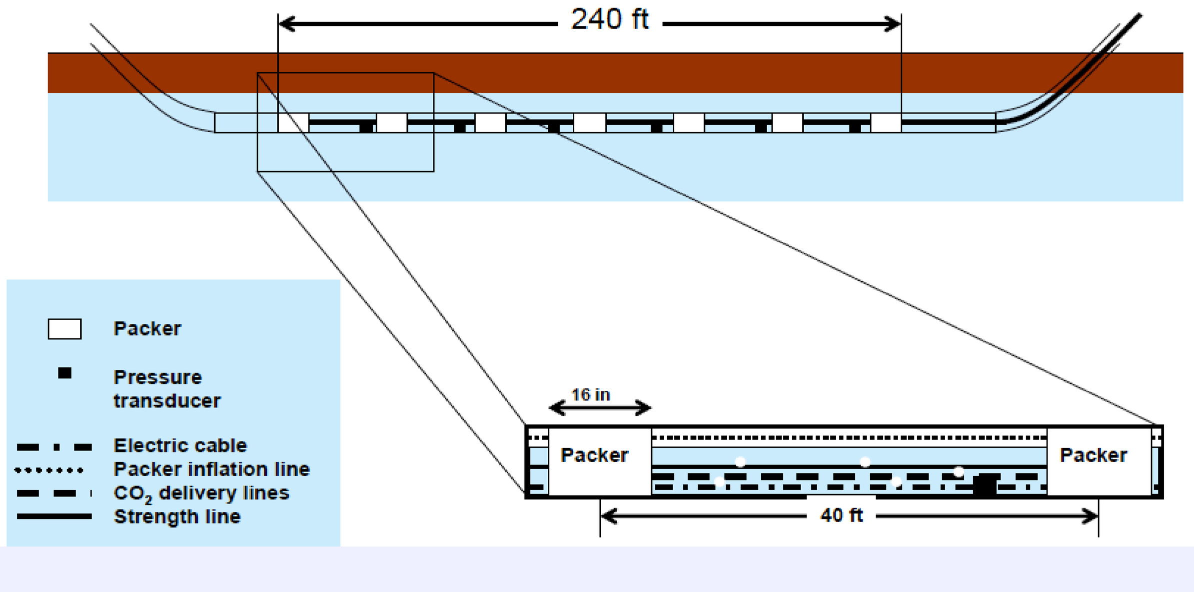
Equipment and Methods

The Site

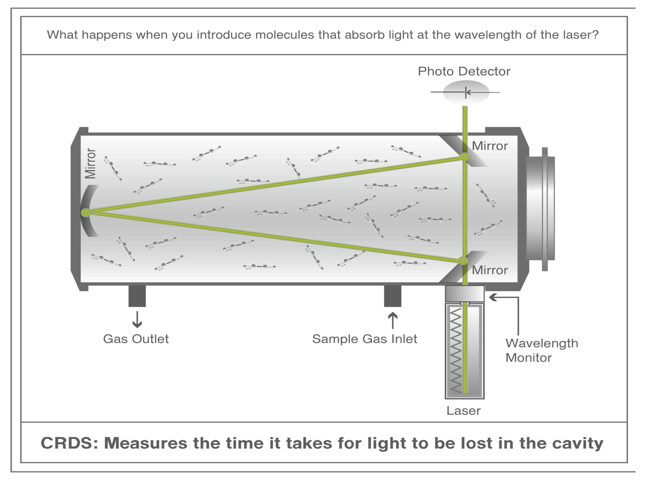
CO2 was released over a 30 day period at a rate of 0.2 tons/day from a 100-meter horizontal well drilled below an alfalfa field at a depth varying between 1-3 meters below the surface. The injection rate is designed to simulate leakage from a mature storage reservoir at an annual rate of between .001 and .01%.



Aerial photo of the site with approximate boundaries of survey area (white) and locations of the beginning and end of the pipe



Schematic of the horizontal well with detail of the packing and CO2 release system (ZERT)



Schematic of the ringdown chamber in a CRDS device (Picarro)

Isotopic Measurements

The isotopic composition of the gas from the tank has a $\delta^{13}C$ signature of approximately -52‰, far more negative than either atmospheric (-8‰) or CO2 from soil respiration (-26‰). These distinct isotopic signatures allow for identification of the CO2 leak through observations of the spatially varying isotopic composition of ground-sourced CO2.

The CO2 isotopic and concentration measurements were taken with a Picarro WS-CRDS analyzer. The instrument measures gas concentrations using scanned cavity ringdown spectroscopy, which makes use of the time profile over which light of a specific wavelength will attenuate as it passes through gas. It allows for the rapid and precise measurement of both total CO2 concentrations and the isotopic abundance of 13-C isotopes in the CO2.

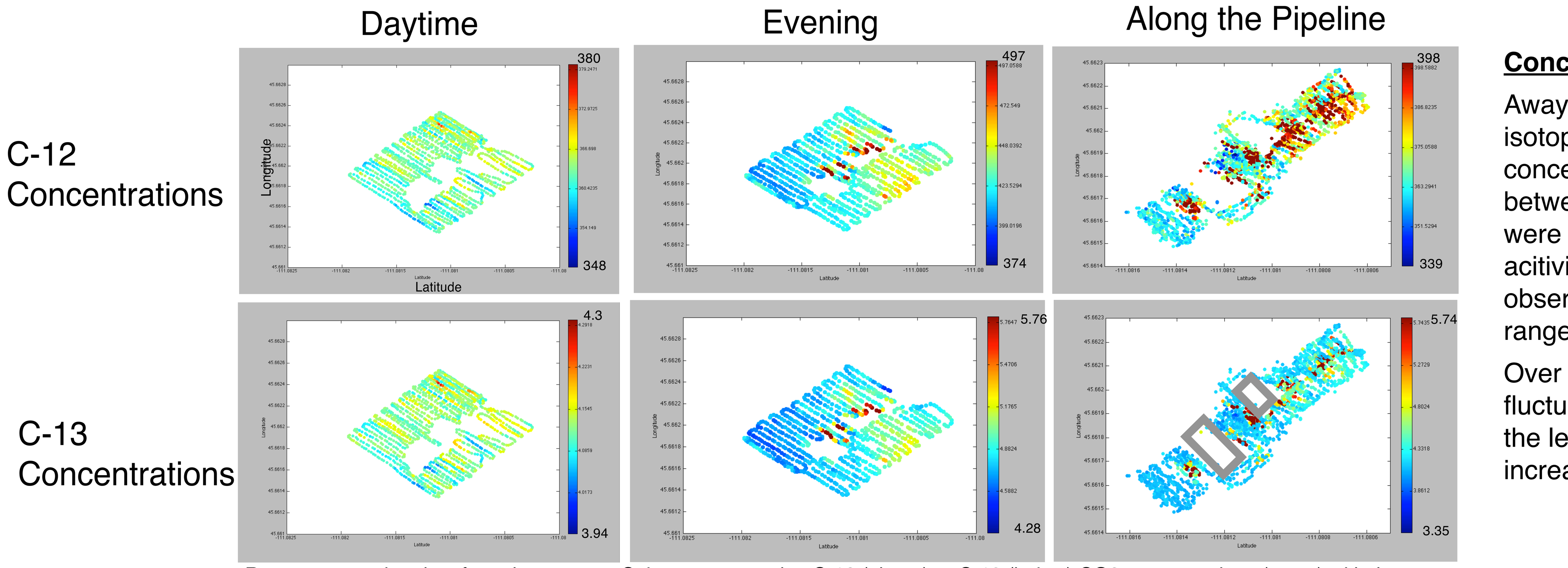
Image showing the inlet of the gas sampler

Jean-Christophe Perrin pulling the cart

Surveys

Surveys of the site were taken by pulling the instrument in a cart at ~ 1m/s along traverses of the site approximately 100m X 100m in dimension. Some areas of the site were not accessible due to the presence of sensitive instrumentation. A 1/8" tube was connected to the gas inlet of the instrument and the inlet port positioned approximately 4 inches above the ground. Position data was logged using a Trimble ProXT GPS reciever and data points were taken about once a second. The surveys were performed both during the day and during the evening when CO2 fluxes due to respiration from the soil were markedly different.

Results and Conclusions



Raw concentration data from the surveys. Colors correspond to C-12 (above) or C-13 (below) CO2 concentrations (ppmv) with the scale given by the color bar on the right side of each image. Dots are locations where each concentration measurement was made. Grey boxes show areas that could not be traversed due to the presence of sensitive equipment.

Concentration Data

Away from leakage sites, CO2 concentrations and their isotopic abundances fell within fairly narrow ranges of concentration. During the day, 12-CO2 concentrations were between 350 and 380 ppmv, while 13-CO2 concentrations were in the range 4.01-4.3 ppmv. At night, when photsynthetic acitivity is less, concentrations go up and 12-CO2 was observed to range from 400-470ppmv, and 13-CO2 in the range of 4.6-5.4ppmv.

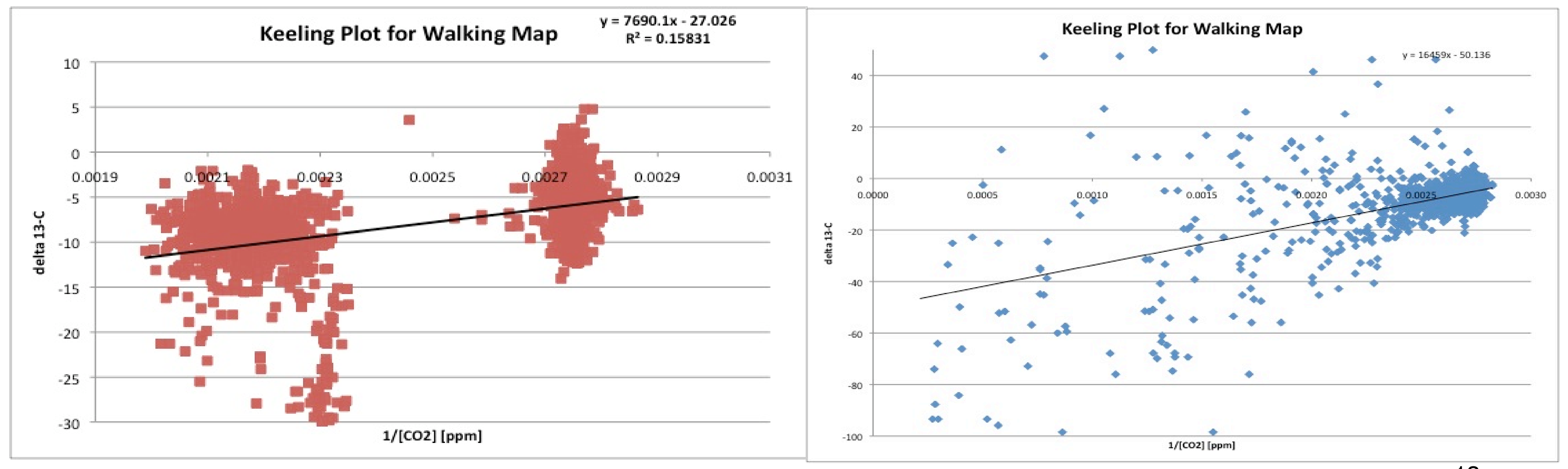
Over the leakage sites, values are markedly higher, but also fluctuate rapidly. It is clear that in this case an identification of the leakage source is possible through observation of increased CO2 concentrations in the proximity of the leakage.

Keeling Plots

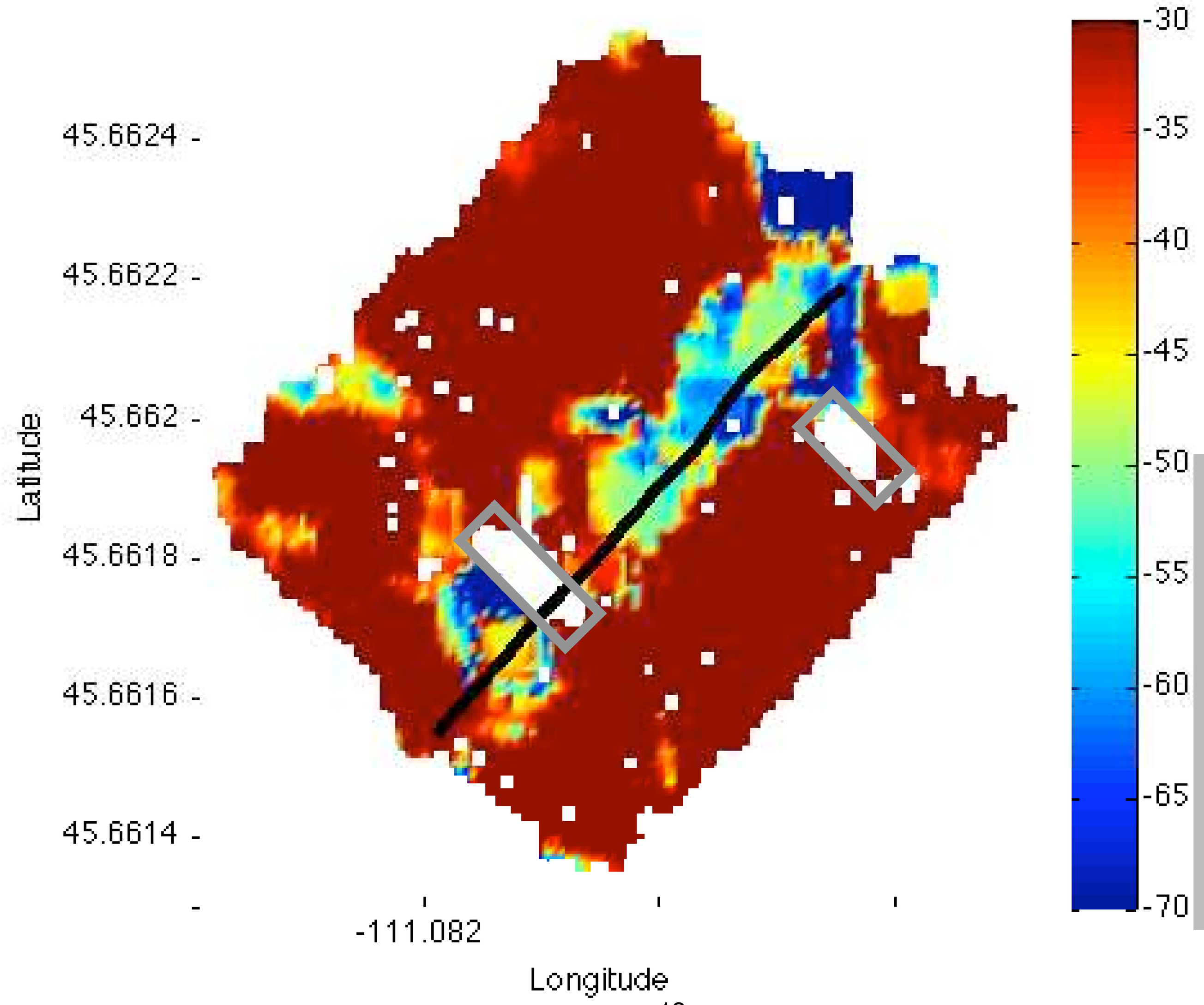
The Keeling plot is used to identify the isotopic signature of a source flux of CO2 entering an ambient or background atmosphere with a constant $\delta^{13}C$ signature. Using simple mass balances, one may derive an equation for the measured $\delta^{13}C$ ($\delta^{13}Ca$) as a linear function with slope proportional to the inverse of the total measured CO2 concentration (Ca) and intercept the $\delta^{13}C$ of the source flux ($\delta^{13}Cs$).

$$\delta^{13}c_a = c_b(\delta^{13}c_b - \delta^{13}c_s)\frac{1}{c_a} + \delta^{13}c_s$$

Measured $\delta^{13}C$ ($\delta^{13}Ca$) as a function of the background CO2 concentration, the source $\delta^{13}C$ ($\delta^{13}Cs$), and the total measured concentration (Ca)

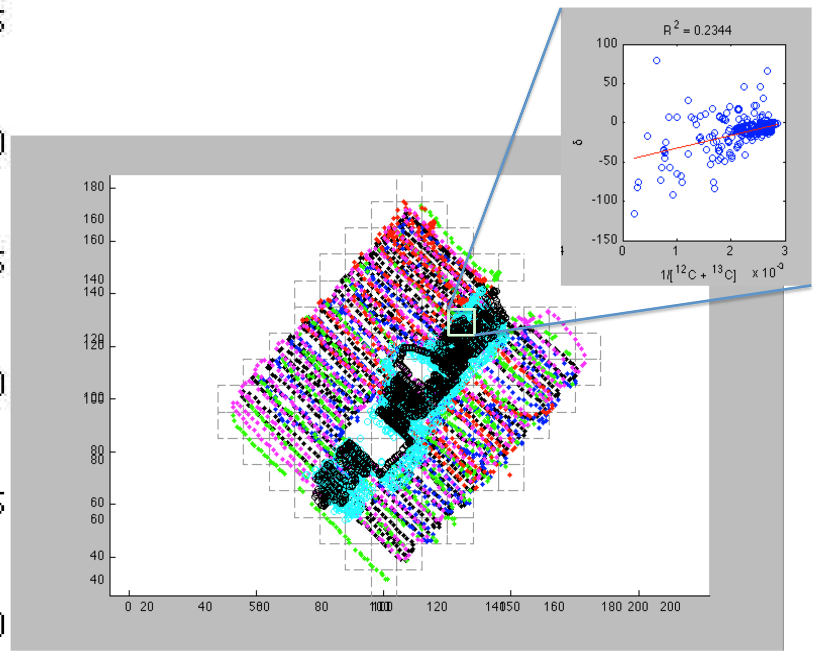


Keeling plots of data from walking surveys taken far from the leakage site (left) and along the pipeline (right). Plotting the measured $\delta^{13}C$ versus the inverse of total CO2 concentration, the $\delta^{13}C$ of the ground sourced CO2 is identified as the y-intercept of the bestfit line, in this case -27‰ for the CO2 away from the leakage and -50‰ for the CO2 over the pipeline.



The $\delta^{13}C$ Map

$\delta^{13}C$ maps show that the CO2 flux from locations where tank-based CO2 was leaking through the surface were characterized by a $\delta^{13}C$ of -40‰ or less whereas locations away from the leakage spots had much higher $\delta^{13}C$ signatures, -30‰ or higher. The results of the surveys show that a site of CO2 leakage at the surface can be readily detected and characterized on the meter scale through rapid mobile surveys. The distinct isotopic signature of the tank-based CO2 allows for a clear identification of the leakage independent of identification based on spatially-varying increases in concentration.



Above: Keeling plot based map for the spatially varying $\delta^{13}C$ signature of CO2 flux from the ground. The image is constructed by using multiple surveys worth of data superimposed and making keeling plots of data within a specific area. Grey boxes show areas that were inaccessible due to the presence of sensitive equipment. Right: Image showing several surveys worth of data on a 10 X 10m grid used for making spatially varying Keeling plots.

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